

TITLE of THE INVENTION

Bio-decomposable polymer composition showing good thermal decomposition

BACKGROUND of THE INVENTION

1. Field of The Invention

This invention relates to bio-decomposable polymer composition showing good thermal decomposition, in which a drop of weight-average molecular is possible to control within 30 % of the initial after treatment of molding and radial sterilization, by adding free radical scavenger to the bio-decomposable polymer.

In this invention, the bio-decomposable polymer is defined as a gentle polymer for organ and environment, after maintaining for a certain period certain shapes and properties both out- and inside organs, hydrolyzing by an enzyme or non-enzyme and disappearing the shapes.

2. Description of The Related Art

The bio-decomposable polymer is composed of natural and synthetic polymers, and an enzyme hydrolyzes almost all natural polymers, in which a collagen composed of polypeptide, is a representative of the natural polymer and hydrolyzed by collagenase. And polyglycoside composing of glycoside combination, is mentioned cellulose, starch, hyaluromic acid, chitin and chitosan. The cellulose is also hydrolyzed by cellulase enzyme.

In spite of a fact that natural polyester produced by a microbe was known as a bio-decomposable polymer since 1920 years, but was not applied for a long time. However, as a result of nowadays progress in bio-technology, many kinds of natural polyesters are researched and developed as bio-decomposable materials, including of poly- β -hydroxybutylate.

On the other hand, many kinds of synthetic bio-decomposable polymers belong to such polymer scopes hydrolyzing by non-enzyme, however, polypeptide such as poly glutamic acid is hydrolyzed by peptide decomposition

enzyme similar to natural poly-peptide.

Almost all synthetic polyester of the bio-decomposable polymers belong to such polymers as poly-glycolic acid, poly-lactic acid or co-polymer of glycolic and lactic acids, hydrolyzing by non-enzyme and frequently applying in clinical use as medical materials, today.

There are many applications of the bio-decomposable polymers employing as medical materials, but restricting within almost surgical use of clinical field such as suture of operation or bone fixation materials. There are employed as many other industrial uses including PLLA film molded products such as a garbage bag, agricultural film, stored bag, or textiles, as PLLA is possible to be decomposed by a microbe under nature environment.

On the other hand, produced method of bio-decomposable polymer is applied by such as production methods as extrusion of heated meltdown, injection, pressed molding in common use as medical and industrial materials. However, heating process is inevitably avoided in record of production.

But a drop of molecular weight inevitably happens in products after heating process, because bio-decomposable polymer generally shows poor heat stability. In addition, sterilization is inevitably necessary different from the industrial use, because bio-decomposable polymer is applied in surgical use of clinical field such as suture of operation or bone fixation materials. Ethylene-oxide gas is generally applied for the sterilization process, because bio-decomposable polymer shows poor durability against radiation exposure. But in this process, ethylene-oxide gas applied for the sterilization, is toxicity in living body, therefore, it is inevitably necessary to remove residual gas after sterilization process, by sucking up long time in order to remove the gas, but impossible to perfectly remove the gas. Present sterilization method by radiation irradiation is employed in many cases of bio-decomposable polymers applied in medical use category as a result. And only specified kinds of bio-decomposable polymers are possibly irradiated, but some strength deterioration

inevitably avoids, caused on decomposition by irradiation.

It is the object of this invention so as to avoid or restrict molecular weight drop in the course of heat treatment process and strength deterioration, caused by sterilization, and fabricating polymer composition by applying the restricted polymer.

SUMMARY of THE INVENTION

In this invention, after wholeheartedly investigation, we propose bio-decomposable polymer composition showing good thermal decomposition, wherein a drop of weight-average molecular controls within 30 % of the initial after treatment of molding and radial sterilization process, by adding free radical scavenger to the bio-decomposable polymer, in order to resolve the above problem.

Bio-decomposable polymer composition of the invention, standing thermal and radial decompositions, is possibly applied for medical and many other industrial uses. Moreover, this processing method is applied for non-bio-decomposable polymer fields such as nylon or polypropylene for sterilization of thermal casting and irradiation.

DETAILED DESCRIPTION of THE INVENTION

For bio-decomposable polymer composition of the invention, the free radical scavenger is selected from the oxidizing resistance agent group consisting of polyphenols, tannic acids, or gallic acids, vitamin group consisting of Vitamin E or Vitamin C, or triarylisocyanulate, by adding the free radical scavenger to bio-decomposable polymer composition, thermal, mechanical and irradiation improve properties.

When the bio-decomposable polymer is heated up until 50-degree Centigrade higher than its melting temperature, radicals generate from the polymer. Moreover, the polymer begins to be deteriorated by oxidizing reaction caused by ambient oxygen. The molecular weight of the polymer is intensely deteriorated by high dose (of 2 to 3 MRad) applied radiation similar in heating, generating radicals in

molecular chains of the polymer, cutting the chains and intensely deteriorating the molecular weight.

Here, in order to prevent the molecular chains from cutting by the generated radicals caused by thermal and irradiation, we can attain our goal, by previously adding the free radical scavenger to bio-decomposable polymer composition in order to catch the generated radicals,

Additional volume of the free radical scavenger is preferably a range of 0.01 to 10wt.%, more preferably a range of 0.01 to 2wt.%, for 100 wt.% of the polymer. If additional volume is less than 0.01 wt.%, it will take many hours before we get desired results. If additional volume is more than 10wt.%, the addition does not have any effect on, but obstruction to.

There is no special method or process for adding and mixing free radical scavenger to the bio-decomposable polymer composition. For example, in a case of adding vitamin E, it is possible not only to direct adding to the polymer in the mentioned volume range, but also at first mixing and solving the vitamin E in organic solvent such as acetone, making a mixture of the polymer and vitamin E by adding and mixing, at final drying up the mixture.

In order to get uniform additional mixture, the bio-decomposable polymer composition is possibly absorbed and formed complex in inorganic compounds such as apatite, zeolite or titanium dioxide.

Heat-treat methods including extrusion, injection and heat pressing are pointed out, as a manufacturing process of the bio-decomposable polymer composition of adding and mixing free radical scavenger. It is preferred that the composition is produced at not 50-degree Centigrade higher than melting temperature of the bio-decomposable polymer, because its temperature is upper limited temperature for generating free radicals. There is no restriction with respect to under limited temperature, but it is preferred to produce at higher temperature than softening point of the bio-decomposable polymer because of view of easy production.

The bio-decomposable polymer composition previously adding and mixing the free radical scavenger is irradiated radiation such as $^{60}\text{Co} - \gamma$ ray and sterilized, applying by ordinary method. It is preferred that radiation is irradiated and produced in dose range of 1.0 to 3.0Mrad. It is not preferred that if the radiation is irradiated less than 1.0 Mrad dose, sterilized effect is poor, and more than 3.0 Mrad dose, molecular weight of the polymer begins to deteriorate.

There is no special rule for produced steps of heating process and sterilized process irradiating radiation. But it is preferred that at first step, heating process is carried out, and next, sterilized process are performed in order to easily produce.

The bio-decomposable polymer of this invention is composed of natural and synthetic polymers, free radicals happen during produced steps of heating process and sterilizing process by irradiated radiation, in which the polymer includes the group consisting of poly-glycolic acid, poly-lactic acid, poly-dioxanon, gelatin, hyaluronic acid, collagen, poly-amino acid, poly-caprolacton, copolymer of lactic and glycolic acid, copolymer of lactic acid and caprolacton, copolymer of glycolic acid and caprolactone, poly-hydroxybutylate, chitin, albumin, or chitosan. Bio-decomposable polymer composition of the invention is possibly applied for medical and many other industrial uses.

By this invention, the bio-decomposable polymer is prevented molecular weight loss from degrading in produced steps of heating process and sterilizing process by irradiated radiation. The high quality bio-decomposable polymer composition is possibly produced.

In conclusion, products of bio-decomposable polymer composition such as suture for operation and bone fixation material are maintained mechanical properties, prevented molecular weight loss from deteriorating and improved several properties, caused of heating process and sterilizing process by irradiated radiation.

Other polymer materials added to the bio-decomposable polymer, such as polyethylene for artificial joint friction

parts, that needs heating process and sterilizing process by irradiated radiation, can be applied by this invented method, in order to prevent molecular weight loss from deteriorating.

EXAMPLE

Followed examples show detailed explanation of this invention, however the invention is not restricted by the examples.

The weight-average molecular weights shown in the examples are measured by Shimazu GPC.

Example 1

After we made about 340 thousand poly-L-lactide (PLLA) material of weight-average molecular by adding 0.1 wt. % Vitamin E (Tocopherol), and molded rod sample of 10cm length and 10mm diameter by injection machine (Nisshou Jushi Ind. Ltd., NS40-A).

While weight-average molecular weight of PLLA rod having no Vitamin E additive declined until about 180 thousand after molding, weight-average molecular weight of PLLA rod having Vitamin E additive showed almost no molecular weight drop of about 330 thousand molecular weight.

Example 2

We spun the thread of PLLA pellet by applying simplified melting spinner that PLLA showed its weight-average molecular weight of about 280 thousand and was added 1.0 wt. % of Vitamin E. The molecular weight after spinning showed about 26 thousand, indicating small molecular weight drops.

On the other hand, PLLA thread adding no Vitamin E additive declined until about 140 thousand, about half molecular weight of initial product after spinning

Example 3

PLLA pellet of weight-average molecular weight of about 280 thousand was made to treated samples composing of 100 parts of titanium dioxide (WakoJunyaku Co.) and 10 parts

of tannin (WakoJunyaku Co.) that absorbed in the titanium dioxide. Next, we fabricated PLLA rod by adding 0.5 parts of treated samples per tannin unit to the PLLA pellet.

The molecular weight after molding the rod showed about 26 thousand, indicating relative small molecular weight drops, while the molecular weight of PLLA rod having no tannin additive declined until about 140 thousand.

Example 4

Copolymer of L-lactide(75 mol%) and caprolactone(25 mol%) of weight-average molecular weight of about 340 thousand was made, added Vitamin E of 0.2 wt.% and spun the thread by applying by simplified melting spinner. Weight-average molecular weight of the copolymer was about 330 thousand and indicated small molecular weight drops.

Example 5

Melt-spun thread gotten by Example 4 was packed in bag laminated by aluminum and polyethylene film and replaced by nitrogen gas, and irradiated and exposed by radial ray(⁶⁰Co - γ ray) of 2.5 Mrad. Weight-average molecular weight of the thread after radiation was about 300 thousand.

Example 6

PLLA pellet of weight-average molecular weight of about 280 thousand was added triarylisocyanulate of 0.2 wt.%, and extruded to rod shape of 2 mm diameter by extruder. Weight-average molecular weight of extruded PLLA slightly increased until 290 thousand.

Further, we made the product vacuum-packing and irradiating, exposing by radial ray(⁶⁰Co - γ ray) of 2.0 Mrad, and getting cross-linked product that showed mechanical properties improved.

Example 7

At first, we fabricated treated specimen composed of 100 parts hydroxy-apatite and 1 part Vitamin E absorbed in hydroxy-apatite. A mixture composed of 100 parts of PLLA pellet of weight-average molecular weight of about 280 thousand was mixed with 30 parts of the treated specimen

in apatite and molded by injector. Molecular weight of PLLA in obtained composite showed almost no molecular weight drop of about 330 thousand molecular weight. After forming the composite by applying hydrostatic pressure type extruder in order to orientate molecular chains, the composite was irradiated by $^{60}\text{Co} - \gamma$ radiation of 2.5MRad and finished PLLA/apatite composite. Molecular weight and mechanical properties of the composite showed about 300 thousand, high tenacity and high modulus, respectively.

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